

APPENDIX C

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(see later page)

TECHNICAL BULLETIN 22/91

LIAL

DETERGENT ALCOHOLS



EniChem Augusta Industriale

LIAL

Primary Alcohols
for Detergent Manufacture
and other Industrial Uses

1. INTRODUCTION

LIAL is the brand name of the high molecular mass primary alcohols produced by EniChem Augusta Industriale in its 80,000 MT/year plant in Augusta (Sicily).

The LIAL family includes four different grades of alcohols, distinguished by their different range of homolog distribution and different average molecular mass.

The numerical suffixes following the brand name LIAL indicate the grade of the product and the length of its alkyl group.

Thus, LIAL 111 is an alcohol with an alkyl group of eleven carbon atoms, while LIAL 123 and LIAL 145 are mixtures of $C_{12} - C_{13}$ and of $C_{14} - C_{15}$ alcohols respectively.

LIAL 125 is obtained by mixing LIAL 123 and LIAL 145 in equal ratio by mass and includes therefore four consecutive homologs.

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2. MANUFACTURE AND STRUCTURE OF LIAL

LIAL are manufactured by hydroformylation of internal n-olefins with a gaseous mixture of carbon monoxide and hydrogen, in the presence of a cobalt hydrocarbonyl catalyst.

Figure 1 shows a simplified block diagram of the process.

After exhaustive separation from the catalyst, the oxo-crude aldehydes are catalytically hydrogenated and converted into alcohols.

The product is then fractionated in a distillation section, where the light and heavy ends are removed.

A final hydrogenation treatment reduces insaturations and carbonyls still present in the raw alcohol to very low levels.

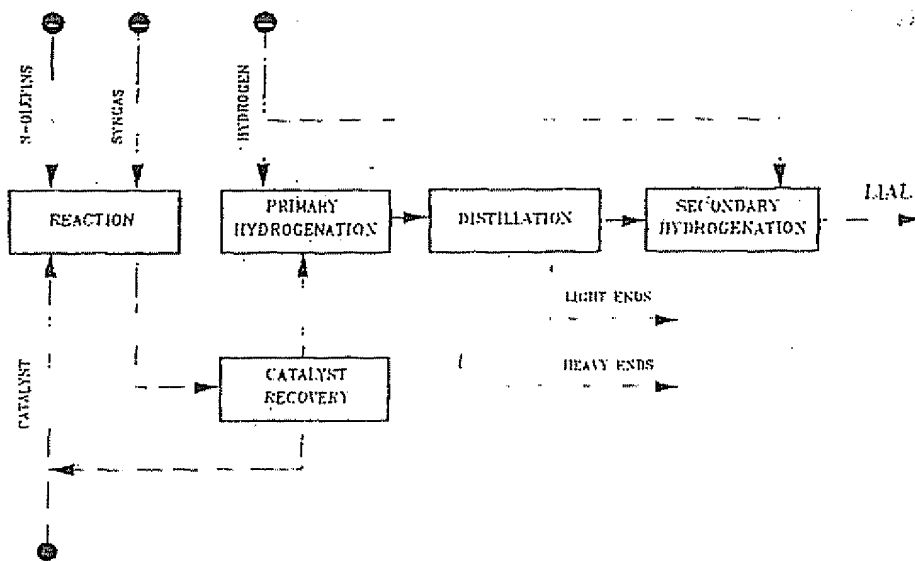


Figure 1 - LIAL: flow-sheet of production process

Due to the chemical structure of the olefin feedstock, the derived LIAL are primary and fundamentally linear alcohols with a carbon atom number increased by one unit compared with that of the parent n-olefins. Seen in greater detail, the alkyl structure of LIAL is a mixture of completely straight chain and monobranched isomers in a ratio very close to one. Figure 2 shows as an example the chain structure of the different isomers present in LIAL 111.

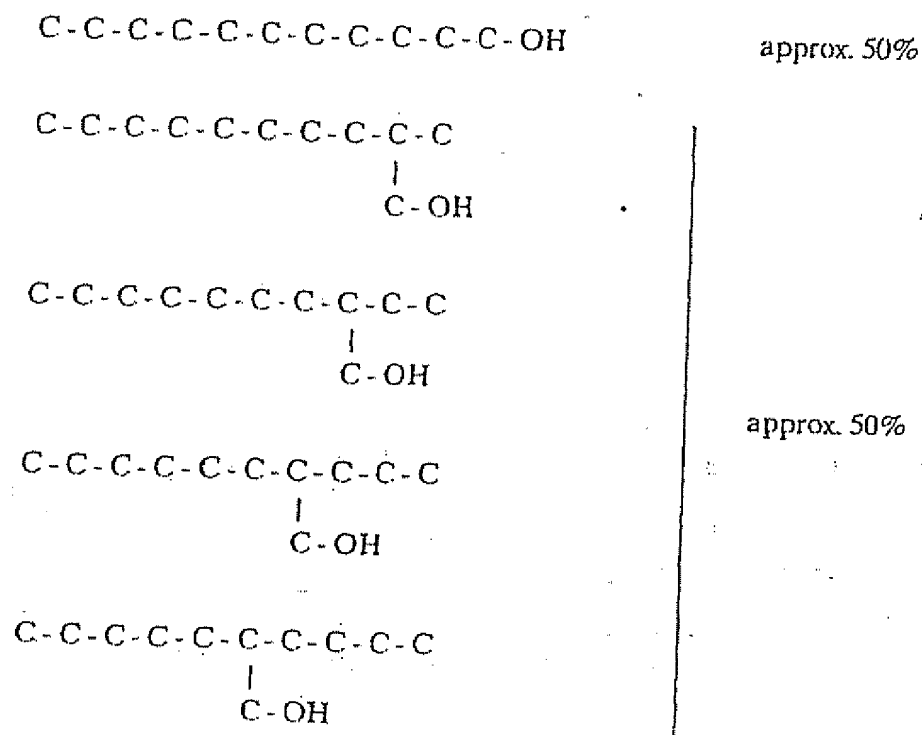


Figure 2 - Structure of LIAL 111

The substantially linear structure of the alkyl ensures the prompt and easy biodegradability of both anionic and nonionic LIAL-derived surfactants.

3. PRODUCT CHARTS

LIAL are high purity colourless liquids with odour very low of its kind. The salient physical and chemical properties that are typical of the LIAL line, the specifications to which these alcohols are customarily produced, and the gas chromatograms obtained with capillary columns are given in Table 1 and in Figures 3 through 6 respectively. All data refers to standard trade products.

The analytical methods employed to describe the products are drawn from two sources:

- ASTM, of the American Society for Testing and Materials, and
- CR, of EniChem Augusta Industriale.

The latter are available in Italian or English upon request.

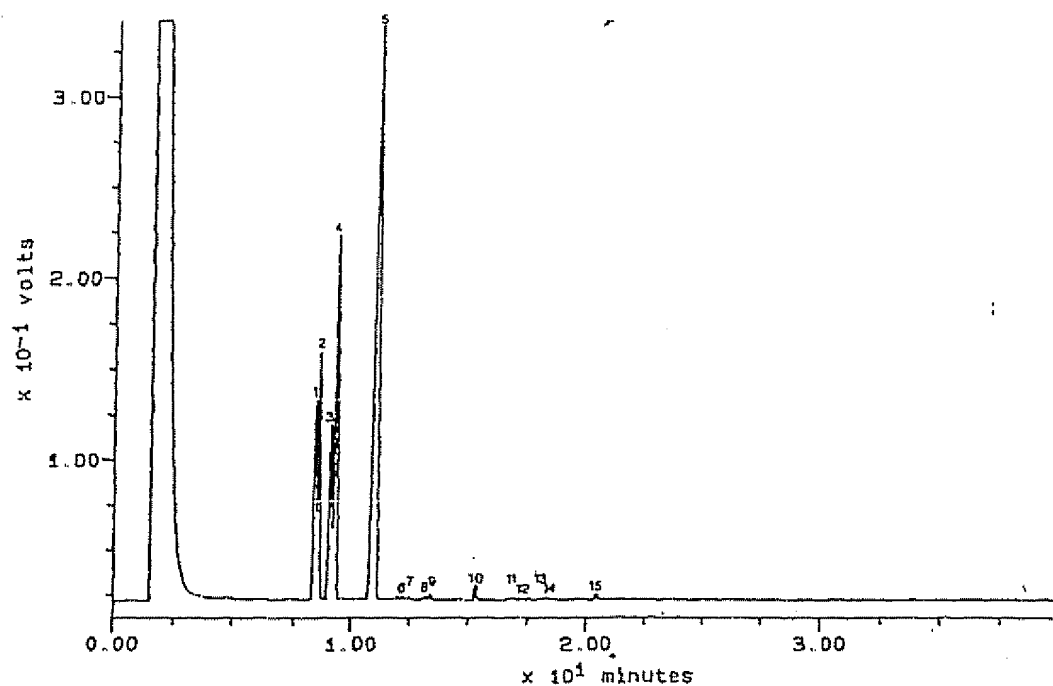
PROPERTY	TEST METHOD	LIAL 111	LIAL 123	LIAL 125	LIAL 145
		typical value	typical value	typical value	typical value
Appearance at 25 °C	--	clear liquid	clear liquid	clear liquid	clear liquid
Colour APIA	ASTM D 1209	5	5	5	5
Density at 20°C (Kg/l)	ASTM D 1298	0.829	0.836	0.836	0.830(*)
Clear Point (°C)	CR 541/12	2	10	12	20
Pour Point (°C)	ASTM D 97	1	5	6	15
Flash Point, PMCC (°C)	ASTM D 93	120	126	132	140
Carbon Distribution (% Mass)	CR 1076				
- C10		2 (a)	--	--	--
- C11		94	0.5 (c)	0.2 (c)	--
- C12		4 (b)	42	20	--
- C13		--	56	31	1 (f)
- C14		--	1.5 (d)	29	42
- C15		--	--	19	36
- C16		--	--	0.8 (e)	1 (e)
Average Molecular Mass	CR 1076	172	194	207	219
Linear Alcohols (% Mass)	CR 1076	50	43	41	39
Monobranched Alcohols (% Mass)	CR 1076	50	57	59	61
Distillation Range at 1.013 bar	ASTM D 86				
- I.B.P. (°C)		239 *	253	261	274
- F.B.P. (°C)		264	277	298	296
Hydroxyl Number (mg KOH/g)	CR 541/8	326	289	273	256
Acid Value (mg KOH/g)	CR 541/4	0.03	0.02	0.03	0.03
Saponification Value (mg KOH/g)	CR 541/7	0.05	0.01	0.02	0.03
Carbonyl Number (mg KOH/g)	CR 541/5	0.08	0.10	0.10	0.20
Bromine Index (mg Br ₂ /100 g)	ASTM D 1491	30	25	30	25
Water (% Mass)	ASTM D 1744	0.04	0.04	0.04	0.04
Hydrocarbons (% Mass)	CR 1076	0.05	0.08	0.10	0.10

PROPERTY	TEST METHOD	LIAL 111	LIAL 123	LIAL 125	LIAL 145
		specification	specification	specification	specification
Appearance at 25 °C	--	clear liquid	clear liquid	clear liquid	clear liquid
Colour APIA	ASTM D 1209	10 max	10 max	10 max	10 max
Flash Point, PMCC (°C)	ASTM D 93	> 110	> 125	> 125	> 125
Carbon Distribution (% Mass)	CR 1076				
- C10		5 max (a)	--	--	--
- C11		90 min	1 max (c)	0.5 max (c)	--
- C12		5 max (b)	38-48	19-25	--
- C13		--	52-62	28-34	2.5 max (f)
- C14		--	3 max (d)	27-33	55-65
- C15		--	--	15-21	35-45
- C16		--	--	1.5 max (e)	3 max (e)
Average Molecular Mass	CR 1076	170-175	192-196	204-209	217-222
Hydroxyl Number (mg KOH/g)	CR 541/8	324-328	287-293	270-276	252-258
Acid Value (mg KOH/g)	CR 541/4	0.05 max	0.10 max	0.10 max	0.08 max
Saponification Value (mg KOH/g)	CR 541/7	0.10 max	0.15 max	0.15 max	0.15 max
Carbonyl Number (mg KOH/g)	CR 541/5	0.10 max	0.15 max	0.25 max	0.30 max
Bromine Index (mg Br ₂ /100 g)	ASTM D 1491	50 max	50 max	50 max	50 max
Water (% Mass)	ASTM D 1744	0.10 max	0.10 max	0.10 max	0.10 max
Hydrocarbons (% Mass)	CR 1076	0.10 max	0.10 max	0.15 max	0.15 max

(*) at 30 °C

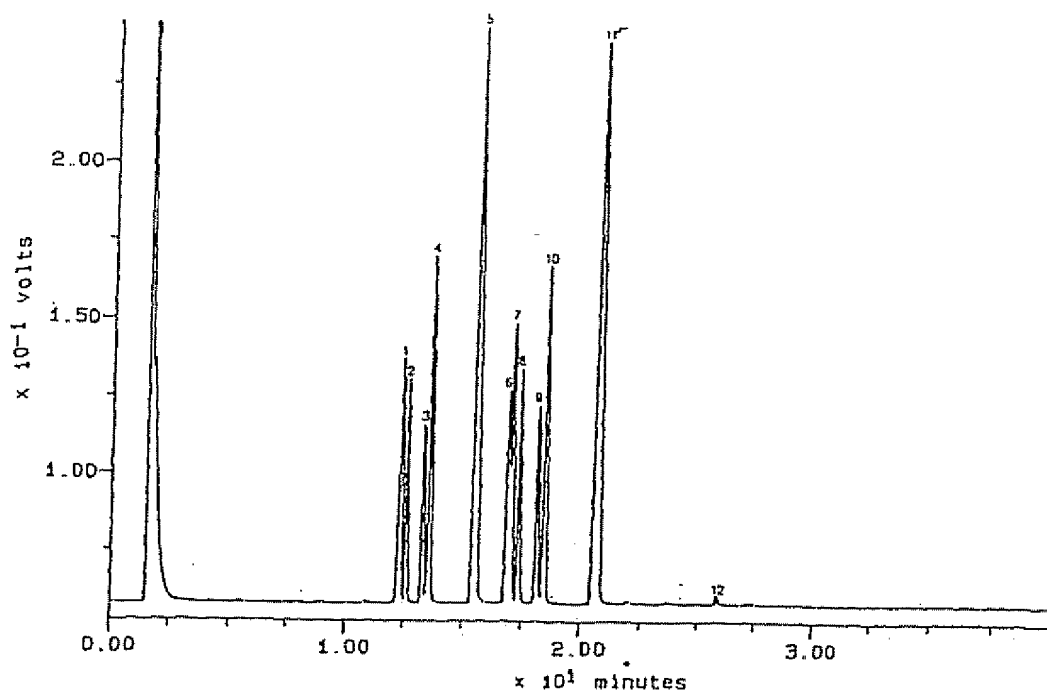
(a) < C11
(b) > C11(c) < C12
(d) > C13(e) < C12
(f) > C15(f) < C14
(e) > C15

Table 1 - LIAL properties: typical values and specifications



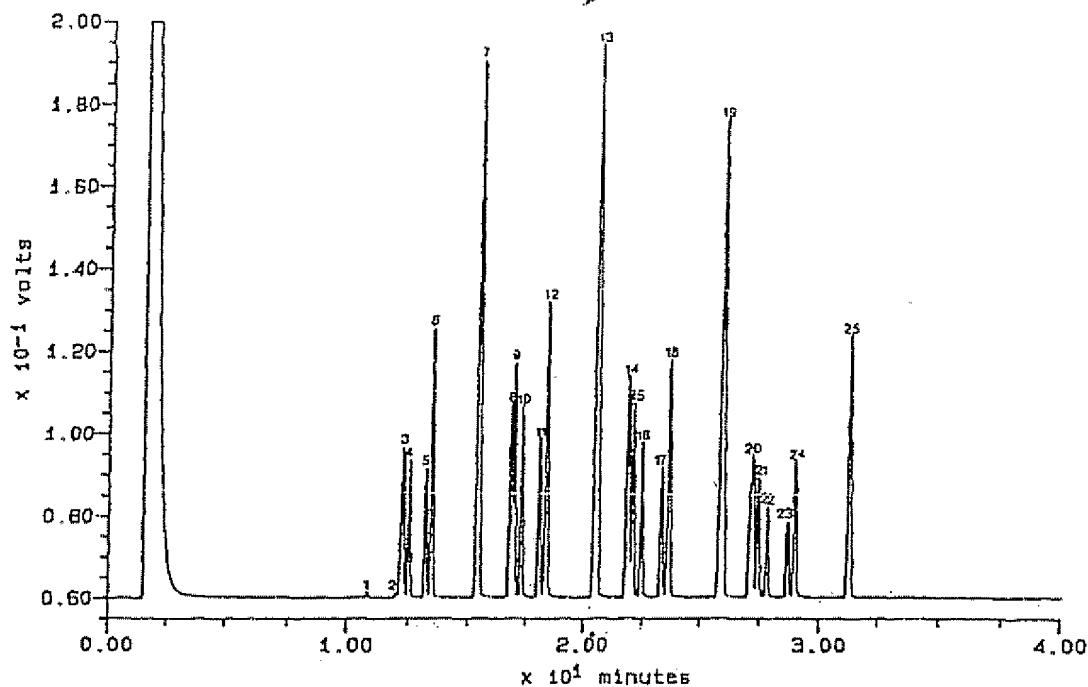
PK#	ID#	Retention (minutes)	Type	Area Percent	Component name
1		1.50	BB		Solvent
2		7.20	BB	0.062	
3	1	8.42	BP	11.195	1-Heptanol,2-Butyl
4	2	8.59	PP	10.057	1-Octanol,2-Propyl
5	3	9.09	FP	9.489	1-Nonanol,2-Ethyl
6	4	9.33	PB	17.545	1-Decanol,2-Methyl
7	5	11.03	BB	49.334	1-Undecanol
8	6	12.16	BP	0.310	1-Octanol,2-Butyl+1-Heptanol,2-Pentyl
9	7	12.43	PB	0.117	1-Nonanol,2-Propyl
10	8	13.11	BP	0.108	1-Decanol,2-Ethyl
11	9	13.35	PB	0.229	1-Undecanol,2-Methyl
12	10	15.27	BB	0.593	1-Dodecanol
13	11	16.73	BP	0.241	1-Nonanol,2-Butyl+1-Octanol,2-Pentyl
14	12	17.22	PP	0.081	1-Decanol,2-Propyl
15		17.59	PB	0.108	
16	13	18.05	BP	0.072	1-Undecanol,2-Ethyl
17	14	18.31	PB	0.133	1-Dodecanol,2-Methyl
18	15	20.43	BB	0.326	1-Tridecanol

Figure 3 - LIAL 111: typical gas chromatogram



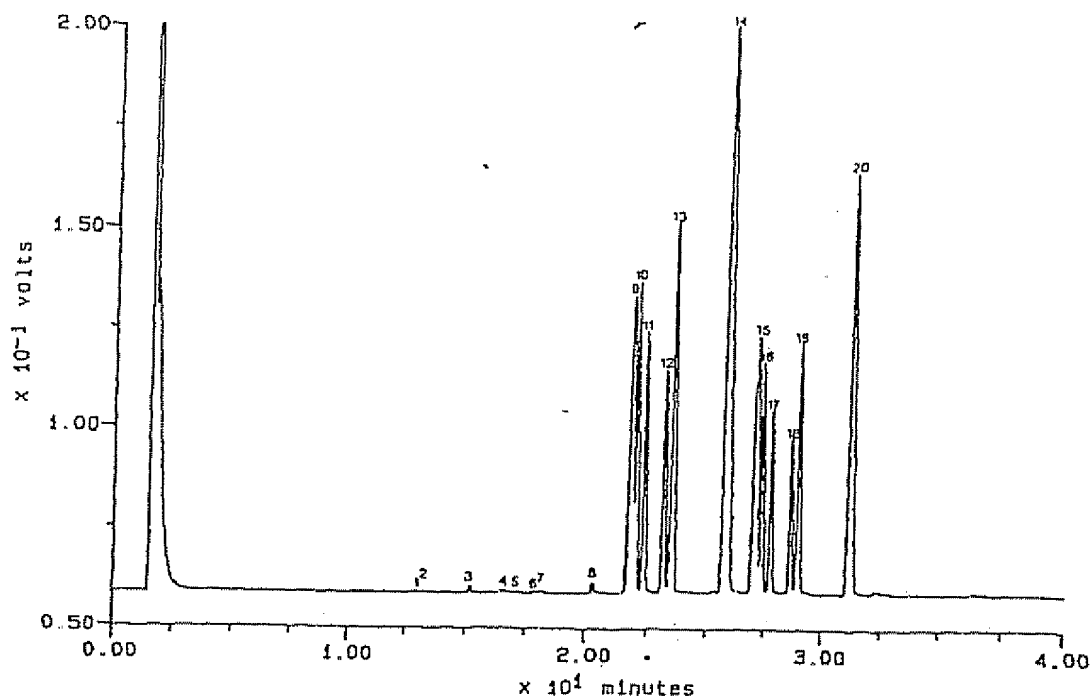
PK#	ID#	Retention (minutes)	Type	Area Percent	Component Name
1		1.54	BB	—	Solvent
2	1	12.38	BP	6.992	1-Octanol,2-Butyl+1-Heptanol,2-Pentyl
3	2	12.62	PB	4.040	1-Nonanol,2-Propyl
4	3	13.29	BP	3.845	1-Decanol,2-Ethyl
5	4	13.59	PB	7.584	1-Undecanol,2-Methyl
6	5	15.63	BB	21.871	1-Dodecanol
7	6	16.96	BP	6.640	1-Octanol,2-Pentyl
8	7	17.13	PP	5.866	1-Nonanol,2-Butyl
9	8	17.43	PB	5.000	1-Decanol,2-Propyl
10	9	18.21	BP	4.644	1-Undecanol,2-Ethyl
11	10	18.55	PB	8.948	1-Dodecanol,2-Methyl
12	11	20.82	BB	24.415	1-Tridecanol
13	12	25.87	BB	0.155	1-Tetradecanol

Figure 4 - LIAL 123: typical gas chromatogram



PK#	ID#	Retention (minutes)	Type	Area Percent	Component Name
1		1.54	BB		Solvent
2	1	10.82	BP	0.097	1-Undecanol
3	2	12.00	PP	0.066	n-Tetradecane
4	3	12.27	PP	2.991	1-Octanol,2-Butyl+1-Heptanol,2-Pentyl
5	4	12.52	PB	1.525	1-Nonanol,2-Propyl
6	5	13.19	BP	1.885	1-Decanol,2-Ethyl
7	6	13.47	PB	3.844	1-Undecanol,2-Methyl
8	7	15.46	BB	11.747	1-Dodecanol
9	8	16.82	BP	3.655	1-Octanol,2-Pentyl
10	9	16.97	PP	3.387	1-Nonanol,2-Butyl
11	10	17.29	PP	2.898	1-Decanol,2-Propyl
12	11	18.07	PP	2.690	1-Undecanol,2-Ethyl
13	12	18.39	PB	5.183	1-Dodecanol,2-Methyl
14	13	20.60	BB	14.148	1-Tridecanol
15	14	21.93	BP	4.918	1-Nonanol,2-Pentyl+1-Octanol,2-Hexyl
16	15	22.13	PP	2.999	1-Decanol,2-Butyl
17	16	22.48	PP	2.464	1-Undecanol,2-Propyl
18	17	23.32	PP	2.191	1-Dodecanol,2-Ethyl
19	18	23.67	PB	4.135	1-Tridecanol,2-Methyl
20	19	25.96	BB	11.972	1-Tetradecanol
21	20	27.23	BP	4.404	1-Decanol,2-Pentyl+1-Nonanol,2-Hexyl
22	21	27.44	PP	1.925	1-Undecanol,2-Butyl
23	22	27.82	PB	1.498	1-Dodecanol,2-Propyl
24	23	28.70	BP	1.269	1-Tridecanol,2-Ethyl
25	24	29.02	PB	2.364	1-Tetradecanol,2-Methyl
26	25	31.29	BB	5.441	1-Pentadecanol

Figure 5 - LIAL 125: typical gas chromatogram



PK#	ID#	Retention Type (minutes)	Area Percent	Component Name
1		1.48 BP	-----	Solvent
2		1.65 PB	-----	Solvent
3	1	13.02 PP	0.123	1-Decanol,2-Ethyl
4	2	13.24 PP	0.044	1-Undecanol,2-Methyl
5	3	15.14 PP	0.245	1-Dodecanol
6	4	16.47 PP	0.130	1-Nonanol,2-Butyl+1-Octanol,2-Pentyl
7		16.72 PP	0.048	
8	5	17.06 PP	0.068	1-Decanol,2-Propyl
9		17.86 PP	0.054	
10	6	18.13 PP	0.119	1-Undecanol,2-Ethyl
11	7	18.66 PP	0.093	1-Dodecanol,2-Methyl
12		19.55 PP	0.040	
13		20.08 PP	0.060	
14	8	20.26 PP	0.371	1-Tridecanol
15		21.18 PP	0.060	
16	9	21.84 PP	9.524	1-Nonanol,2-Pentyl+1-Octanol,2-Hexyl
17	10	22.06 PP	5.793	1-Decanol,2-Butyl
18	11	22.41 PP	5.014	1-Undecanol,2-Propyl
19	12	23.25 PP	4.529	1-Dodecanol,2-Ethyl
20	13	23.63 PP	8.926	1-Tridecanol,2-Methyl
21		25.30 PP	0.178	
22	14	25.98 PP	23.207	1-Tetradecanol
23	15	27.21 PP	9.168	1-Decanol,2-Pentyl+1-Nonanol,2-Hexyl
24	16	27.43 PP	4.088	1-Undecanol,2-Butyl
25	17	27.79 PP	3.370	1-Dodecanol,2-Propyl
26		28.42 PP	0.118	
27	18	28.66 PP	2.908	1-Tridecanol,2-Ethyl
28	19	29.00 PP	5.724	1-Tetradecanol,2-Methyl
29		30.33 PP	0.057	
30		30.56 PP	0.102	
31	20	31.32 PB	15.657	1-Pentadecanol
32		32.36 SV	0.160	

Figure 6 - LIAL 145: typical gas chromatogram

4. ENVIRONMENTAL IMPACT AND SAFETY

4.1. BIODEGRADABILITY

Fundamental requisite of an alcohol used to produce surfactants is that its derivatives be biodegradable.

LIAL-based anionic and nonionic surfactants fully comply with the specific standards set by EEC Directives 82/242 and 82/243, and those of Italian Law n° 136 of 26-4-83.

All these LIAL-derived products are, in fact, over 90% biodegradable; according to testing procedures established by the Organization for Economic Cooperation and Development (OECD).

4.2. ACUTE ORAL TOXICITY

Tests in rat performed with the B-1 method described in EEC Directive 84/449 showed low levels of acute oral toxicity for all grades of LIAL (Table 2).

ALCOHOL	LD ₅₀ mg/Kg (rat)	
	Male	Female
LIAL 111	> 5000	> 5000
LIAL 123	> 5000	> 5000
LIAL 125	> 5000	> 5000
LIAL 145	> 5000	> 5000

Table 2 - Acute oral toxicity in rat

4.3. ACUTE EYE IRRITATION

The evaluation of mucosa-irritating properties was determined in albino rabbit using the procedures prescribed by EEC Directive 84/449 under method B-5. The results obtained (Table 3), indicate only a moderately positive response. In all the cases these phenomena of slight irritation were seen to be rapidly reversible.

ALCOHOL	Iris	Cornea	Conjunctiva	
			Reddening	Chemosis
LIAL 111	0	0	< 2	1.3
LIAL 123	0	0	< 2	1.5
LIAL 125	0	0	< 2	1.5
LIAL 145	0	0	< 2	1.5

Table 3 - Acute eye irritation in albino rabbit

4.4. PRIMARY SKIN IRRITATION

Skin irritation tests were performed in albino rabbit with the procedures prescribed under method B-4 of EEC Directive 84/449.

The experimental results, shown in Table 4, indicate moderately acute irritating effects for LIAL.

ALCOHOL	Edema	Erythema and eschar
LIAL 111	< 2	2
LIAL 123	< 2	< 2
LIAL 125	< 2	< 2
LIAL 145	< 2	< 2

Table 4 - Primary skin irritation in albino rabbit

4.5. ALLERGIC SKIN SENSITIZATION

All four grades of LIAL were tested, using the Kligman-Magnusson method in Guinea pig, for the existence of any sensitizing properties.

The procedures employed were those described under method B-6 of EEC Directive 84/449.

The results exclude any risk of allergic sensitization arising from contact with any grade of LIAL.

5. PHYSICAL PROPERTIES

5.1. DENSITY

The variations in absolute density of the various grades of LIAL versus temperature, in the range between 20 and 50°C, are shown in Figure 7. The readings were taken with a precision digital density-meter, DMA model, produced by PAAR.

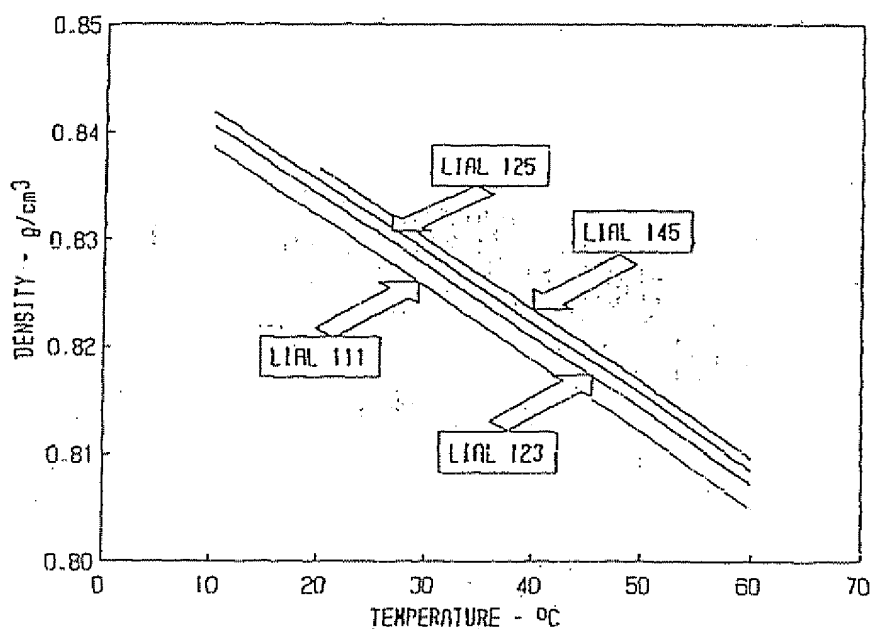


Figure 7 - LIAL: absolute density vs. temperature

5.2. VISCOSITY

Figure 8 shows the kinematic viscosity of LIAL versus temperature. Measurements were taken with a Cannon-Fenske viscometer and cover a span of practical concern, ranging from pour point to 50°C.

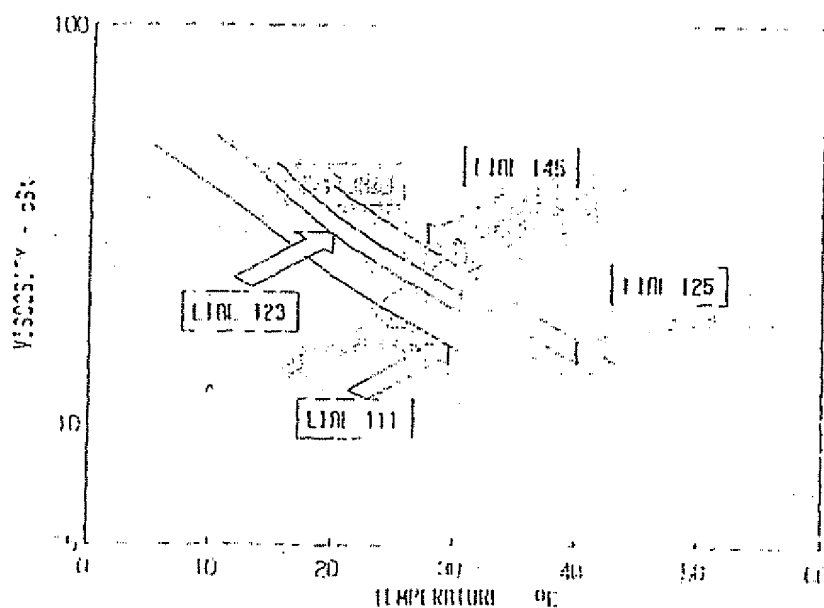


Figure 8 - LIAL: absolute viscosity vs. temperature

5.3. REFRACTIVE INDEX

The refractive index for LIAL within a temperature range of 20 to 50°C is shown in Figure 9.

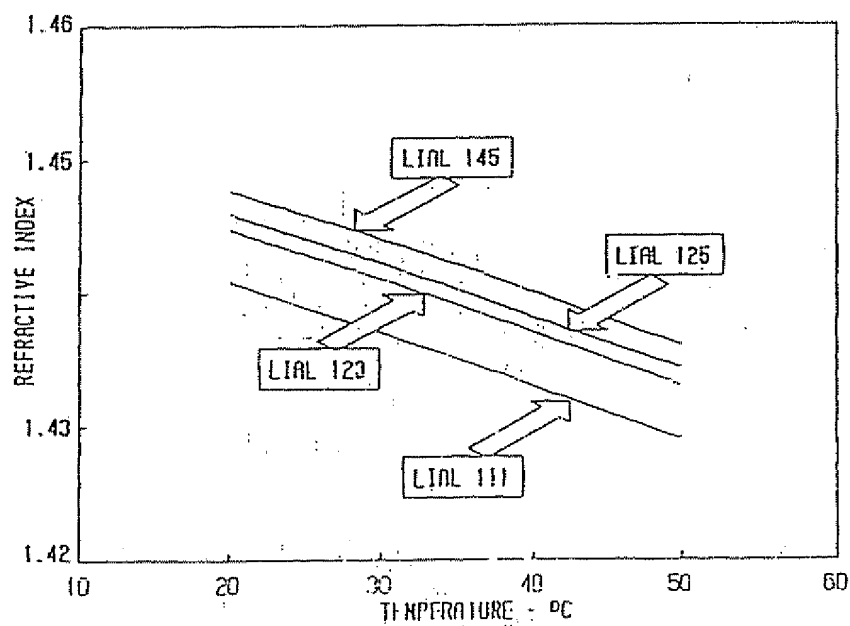


Figure 9 - LIAL: refractive index vs. temperature

5.4. LIAL/WATER SYSTEMS

The solubility of water in LIAL is very limited and little influenced by temperature, at least in the temperature range of 10 to 60°C.

At room temperature the solubility of water in alcohols is, in fact, on the order of 1 to 1.6% (Figure 10).

The solubility of alcohols in water, determined only at 20°C, is less than 10 ppm.

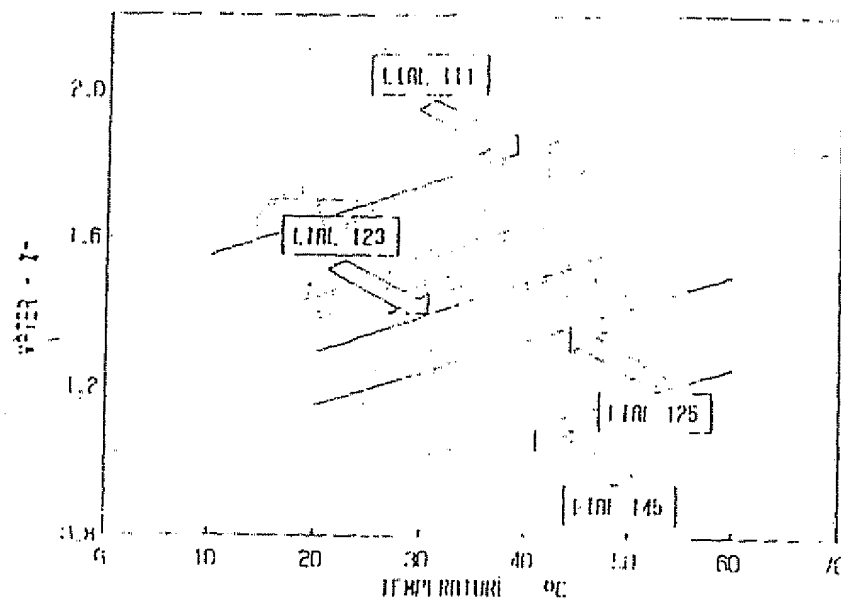


Figure 10 - LIAL: water solubility vs. temperature

5.5. MISCIBILITY WITH ORGANIC SOLVENTS

LIAL mix readily, even at room temperature, with the more common organic solvents.

Table 5 shows the aspects of 1:1 mixtures (by volume) of the four grades of LIAL with a series of organic solvents.

Of all the solvents tested only ethylene glycol failed to form a mixture.

SOLVENT	LIAL 111	LIAL 123	LIAL 125	LIAL 145
Ethyl acetate	1	1	1	1
Ethanol	1	1	1	1
Methanol	1	1	1	1
Isopropanol	1	1	1	1
Ethylene glycol	2	2	2	2
Acetone	1	1	1	1
Benzene	1	1	1	1
Toluene	1	1	1	1
Hexane	1	1	1	1
Decane	1	1	1	1
Chloroform	1	1	1	1
Methylene chloride	1	1	1	1

Table 5 - Miscibility of LIAL with organic solvents; ratio 1:1 by volume at room temperature
 1 = Homogeneous solution 2 = Two-phase system

6. APPLICATIONS

The excellent physical and chemical properties of all grades of LIAL make them attractive products for applications in numerous industrial sectors.

LIAL can easily be reacted with ethylene oxide, following conventional condensation techniques, to produce non-ionic surfactants employed in detergent formulations and in other industrial applications.

Anionic surfactants, such as alkylsulfates and alkylethersulfates, can be manufactured by sulfation of LIAL or of their ethoxylated derivatives (LIALET) with air-diluted SO_2 in thin-film reactors, or with chlorosulfuric acid in both continuous and discontinuous equipments.

These surfactants are employed in the manufacture of detergents and toiletries and as industrial auxiliaries.

LIAL are particularly suited for the synthesis of mono and polycarboxylic acid esters, used in the plasticizer, lubricant and textile sectors.

LIAL are also employed as co-solvents and emulsifiers in printing inks.

7. TRANSPORT AND STORAGE

LIAL are stored in stainless steel or aluminum tanks.

Because of their relatively low pour point - between 0 and 15°C, depending upon the grade - LIAL present only minor problems of storage during the winter months.

When outside temperatures make it advisable to heat the product, heating should not exceed 45°C and hot water systems are to be preferred.

To prevent oxidation during prolonged storage, it is recommended that the product be kept under nitrogen and, if possible, at room temperature.

LIAL alcohols are generally supplied in bulk by tanker, tank truck, or tank container.

They may also be delivered in drums of approximately 215 liter capacity.

The chemical, physical and toxicological properties of all types of LIAL classify these products as non-hazardous substances for transport by ship (IMO), rail (RID), or road (ADR).

According to Annex II to the 73/78 MARPOL International Convention, LIAL 111, LIAL 123 and LIAL 125 can be included in category B with regard to the precautions to be taken for the washing of the tanks after delivery, when shipping the products by sea, while LIAL 145 falls in Appendix III (non-harmful products).

8. HANDLING AND FIRST AID

LIAL alcohols present low levels of acute oral toxicity and are only moderately irritating.

Consequently, prolonged or repeated contact with the skin and mucosa should be prevented.

Protective clothing, Neoprene gloves and anti-splash facial mask or goggles should be worn when handling these materials.

In the event of contact, contaminated clothing should be removed and the part concerned flushed with abundant water.

If the product is accidentally swallowed, vomiting should *NOT* be induced, to avoid any risk of the product being inhaled.

Immediate medical attention should be sought.

Due to their high flash point, LIAL are not classified as flammable substances.

In the event of accidental spills, inert materials should be used to absorb the product and then sent to an incineration plant.

The information and data presented in this bulletin represent our best knowledge of the products concerned, but the Company accepts no responsibility for their derivatives, since the production and use of these are not under our direct control. Nor should any information or data supplied herein be construed as encouraging the use of our products in infringements of any patent rights of manufacture or applications.

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